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AN INSTRUMENT FOR SIMULTANEOUS MONITORING NOx AND SO2 IN STATIONARY SOURCES

Huel C. Tucker, et al

Monsanto Research Corporation

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by

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ABSTRACT

A Monsanto Model 3409 Chemiluminescent Ambient Air Monitor was converted to a two-channel configuration for simultaneously monitoring NO_x and SO_2 in stack gases. Channel separation was obtained by means of narrow-band optical filters. The analog sample-hold part of the automatic zero circuit was replaced by a digital memory circuit. A permeation dryer was included to remove water from the sample. The atomic oxygen source was changed to an ozone generator-thermal decomposition configuration, which failed to provide sufficient oxygen for SO_2 or NO_2 analysis. A microwave oxygen generator provided adequate quantities of oxygen but was rejected because of its unreliability.

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SECTION I

INTRODUCTION

Three major air pollutants are NO, NO_2 and SO_2. Each may be monitored with available commercial instruments. However, no one instrument is capable of analyzing for all three simultaneously. Simultaneous monitoring of all three pollutants requires two or three instruments depending on whether one of them has the capability to directly monitor NO_x, which is the sum of the NO and NO_2 present. Since NO and NO_2 are usually lumped as NO_x, the Environmental Protection Agency (EPA) deemed it to be desirable to develop an instrument to simultaneously monitor SO_2 and NO_x for coal-fired stack emission monitoring.

Previous work in the area of chemiluminescence indicated that the reaction of nitric oxide with ozone could be used in relatively straightforward equipment to measure ambient air levels of NO and NO_2. There are a number of NO_2-to-NO converters in use with such ambient air equipment.

Work in the stationary source area was somewhat complicated by the presence of side reactions that can create or destroy NO or NO_2 in these converters.

The work by G. W. Wooten using microwave-produced atomic oxygen instead of ozone indicated that the reaction

$$NO_2 + O \longrightarrow NO + O_2$$

could be used instead of an external converter to monitor total NO_x. Analogous SO_2 chemiluminescent reactions could also be used to measure SO_2 at the same time.

The potential desirability of a dual SO_2-NO_x monitor for certain stationary sources prompted this contract effort. The modification of an experimental chemiluminescence instrument which was designed for low-level NO_x analysis was decided upon as the most expedient approach to the design of such a dual analyzer. The design goal was to develop an instrument for continuously and simultaneously monitoring NO_x and SO_2 at high levels at remote locations with minimal attention from the operator.

Evaluation of the original instrument showed that the analog sample hold circuits used for zero drift correction were not adequate over long time periods. With the recent advances in digital integrated circuitry in terms of functions and cost, we decided to rework the auto-zero circuitry to use digital components.

Concurrently with the initiation of this program, a sample drying system based on selective water permeation became commercially available. Since removal of condensable water was required for the proper operation of the modified instrument, we undertook to incorporate this new dryer into the sampling system.

SECTION II

RESULTS OF EXPERIMENTAL WORK

The ability of the permeation dryer to selectively remove water from a sample stream was confirmed. However, no effort was made to establish the operating parameters and their limitations.

The automatic zero circuit employing a digital memory was successfully demonstrated. This technique extends the usefulness of all-electronic automatic zero circuitry to include applications requiring memory retention times measured in days or even weeks as opposed to the 10 to 15 minute maximum memory retention time of analog memories.

All attempts to simultaneously measure NO_x and SO_2 using an ozone generator with a thermal decomposition chamber to generate atomic oxygen failed. The response of the instrument to NO was adequate and relatively easy to achieve. The response to NO_2 was inadequate for a measuring circuit having no background noise compensation. NO_2 response was difficult to obtain and required that all parameters be optimized. No response to SO_2 was observed when generating oxygen by this method. It was not established if the response existed or if it was merely hidden in the noise of the system. It was established that the response to NO was destroyed by the introduction of small amounts of SO_2.

The previous work where response to SO_2 and NO_2 was reported was confirmed by a test using a microwave generator and a cavity to generate atomic oxygen. Again, the response to NO was easy to obtain. An adequate response to SO_2 was obtained only by careful and methodical optimization of all

parameters of the reaction chamber. No effort was made to explain the effects of the various parameters.

SECTION III

CONCLUSIONS

A chemiluminescence instrument based on atomic oxygen to simultaneously monitor stationary emission sources for NO_x and SO_2 is impractical with the present state of the art.

Further clarification of the requirements of the chemiluminescence reaction of atomic oxygen with various compounds such as NO_2 and SO_2 is required before any serious consideration can be given to further development of such an instrument.

Although the instrument can be made to function adequately over a short time period by using microwave excitation to generate atomic oxygen, the mechanical instability of the microwave cavity-to-oxygen line system, the projected short life of the microwave tube, and the uncertainties related to maintaining a plasma discharge over a long period of time make that approach unacceptable for a continuous monitor.

Either the ozone generator/thermal decomposition method for making atomic oxygen failed to produce sufficient oxygen, or an unknown reaction between SO_2 and another compound present had a quenching effect on the chemiluminescence reaction. The saturation effect observed with NO_2 indicates that the NO_x measurement can be made in the absence of SO_2 by using a second photomultiplier to compensate for background variations by limiting the flow of the sample into the reaction chamber to keep it within the linear range.

The successful application of a digital memory to an automatic zero circuit represents a significant advance in the state

of the art pertaining to programmed field instruments. It can replace high maintenance servo systems in almost any application where the inherent drift of an analog memory is unacceptable. It may also be useful as a long-term sample-and-hold amplifier.

SECTION IV

TECHNICAL DISCUSSION

DESIGN

The overall design goals were outlined by parts A and C of the following Scope of Work statement, included as Exhibit A in the contract:

"A. The contractor shall modify the existing Monsanto Model 3409 ambient air NO_x monitor to simultaneously measure stationary source SO_2 and NO_x emissions in the following ranges:

SO_2 - 0-200 ppm, 0-500, 0-1000, 0-3000 ppm

NO_x - 0-200 ppm, 0-500, 0-1000, 0-3000 ppm

The unit shall have equivalent responses to NO and NO_2 or mixtures thereof without the use of a conversion device.

B. Tasks required in this conversion include, but may not be limited to:

1. Replacement of differential signal processing circuits and replacement with two independent channels including independent automatic zero correction circuits and manual span adjustment for both channels.

2. Removal of discharge atomic oxygen generator and replacement with ultraviolet ozone generator with small thermal decomposition furnace downstream (1" diameter, 2" long, 800°C) or microwave generator.

3. Replacement of reaction chamber with two port chamber for simultaneous SO_2 and NO_x measurements.

4. Replacement of optical filter on second photomultiplier with filter centered at 3510 Å, ½ width 50 Å.

5. The unit shall retain the internal automatic zero correction and calibration functions.

C. The contractor shall provide a sampling system suitable for operation at a coal-fired steam electrical power plant. This sytem shall include particulate removal and other sample preconditioning as required by the covered prototype.

D. The contractor shall calibrate the instrument for SO_2, NO and NO_2 in the specified ranges and establish interference ratios for 500 ppm CO, 3% O_2, 100 ppm C_2H_6, 10% H_2O, 15% CO_2, 100 ppm N_2O, and 500 ppm NH_3.

E. The converted monitor and sample system shall be deliverable. The contractor shall document and blueprint all changes. The contractor shall provide fifty (50) copies of a design and operation manual and a set of engineering drawings which will be sufficient to enable the manufacture of items of equipment furnished under this contract (other than components or items of standard commercial design or items fabricated heretofore) by a firm skilled in the art of manufacturing items of equipment of the general type and character of the items or equipment furnished under this contract or a set of flow sheets and engineering drawings which will be sufficient to enable performance of any process developed under this contract by a firm skilled in the art of practicing processes of the general type and character of good process. Such set or sets of drawings and flow sheets shall be reproducible copies incorporating all changes made in the equipment or process in the form in which it was delivered to the Government."

Parts B, D and E in the above statement pertain to more specific details to be included in the overall design. Design decisions were based on this statement but were influenced by additional information supplied by the contract monitor. The design goal of up to 3000 ppm of each NO_x and SO_2 was modified to 3500 ppm sum of NO_x and SO_2 on the assurance of the monitor that that capability would be sufficient.

Sampling System

The requirements of the sampling system were set forth in parts C and D of the Scope of Work statement, above. Further clarification by the contract monitor established the need for removing much of the water from the sample at the point of exit from the stack to prevent condensation as the water-laden sample gas cooled enroute to the analyzer. Because of the highly reactive nature of NO_2 and SO_2, any condensation in the sample system would have a drastic effect on these analyses. At the recommendation of the monitor, a permeation dryer was obtained and tested for its effects on SO_2 and NO_2. Simple test procedures were used where 3502 ppm SO_2 and 4350 ppm NO_2 were passed through the dryer and analyzed to determine any changes in the concentrations. There was no detectable change in SO_2 and no more than 2% change in the concentration of NO_2 where the water content of the drying gas was held low. However, it was found that where the water content of the drying air was high, the effect on the concentrations of the SO_2 and NO_2 at the exit of the dryer was drastic in that much of the SO_2 or NO_2 was not passed by the dryer.

A sampling probe was designed utilizing a Model PD-500-40 permeation dryer purchased from Permapure Products, Inc. With reference to the schematic shown in Figure 1, the sample gas is pulled through the permeation tube via a coarse filter at the end of a 6 ft long, 1/2 inch stainless steel pipe designed to be inserted into a stack. After exiting the dryer, the dry gas is routed through flexible tubing to the analyzer. Dry air, obtained from a bottled supply or through a dryer, is pulled through the vacuum compartment via a valve, V1, by pump, P1, and discharged through a solenoid valve, SV2, to

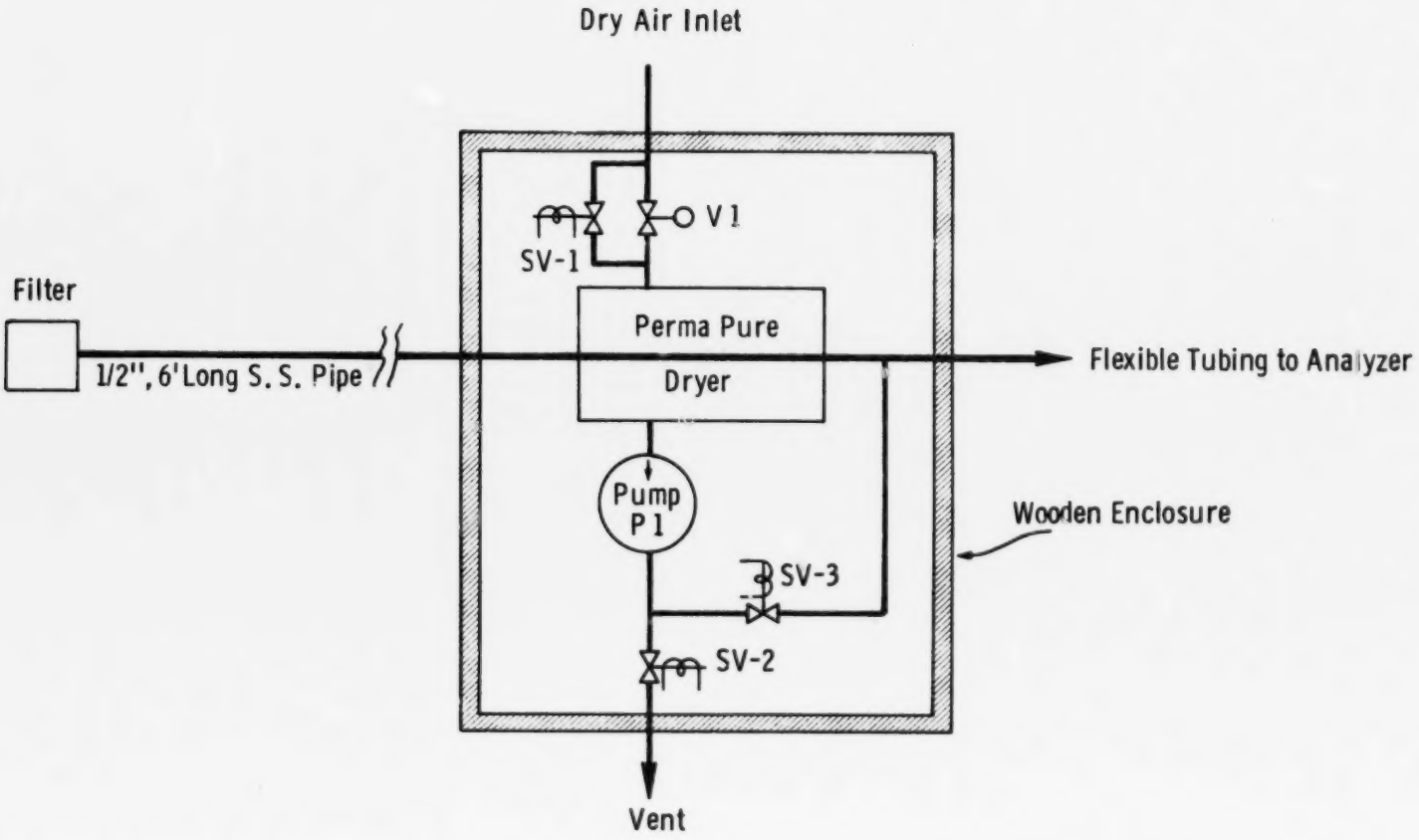


Figure 1. Sample Probe Schematic

atmosphere. During the "zero" and "standard" cycles, where a bottled zero or standard gas is being accepted by the analyzer, the tubing is blocked and SV2 closes, SV1 and SV3 open, routing the effluent from pump, P1, in a reverse direction through the permeation tube, probe, and filter. This procedure should remove some particles collected on the filter, thereby minimizing the maintenance required for cleaning it.

Oxygen Generator

The design of the oxygen generator was the most critical phase of the project. The two approaches that were considered feasible were (1) the direct disassociation of O_2 using microwave power and (2) the indirect method of generating ozone and thermally decomposing it. A survey of the ozone generators available revealed that only the first method could produce sufficient concentrations of atomic oxygen to accommodate the high concentrations of pollutants expected. However, agreement was reached with the contract monitor that, considering the present state of the art, the solution of the problems to be incurred in the use of a microwave generator in an instrument of this type where continuous, unattended operation was required was beyond the scope of this project.

An investigation revealed that commercial ozone generators were available. Previous work reported that linear results could be obtained by the ozone/thermal decomposition methods to well over 100 ppm NO_x in N_2. The reported signal level at 100 ppm was adequate to provide a readout for the instrument. Therefore, it was decided to design the oxygen generator using the ozone/thermal decomposition method, and

to dilute the sample gas with air to reduce the pollutant concentration to an acceptable level. An Orec Model 03V5-OM ozonator was purchased and a thermal decomposition chamber designed to provide atomic oxygen. The generator is shown in Figures 2 and 3.

Reaction Chamber

The reaction chamber was designed to mix the sample stream with a stream containing the atomic oxygen. It provides observation ports at opposite ends for two photomultipliers. There is a relatively long path for the mixed stream to exit to the vacuum pump as shown in Figures 4 and 6. The chamber is housed in a light-tight box as shown in Figure 5. The flow rates of both sample and oxygen/ozone are controlled by stainless steel needle valves to provide the proper mixing. A by-pass valve provides control of the pressure in the chamber.

Pneumatic Circuit

The plumbing for the instrument is shown by the schematic in Figure 6. All fittings, tubing, valves, etc., are stainless steel, glass, quartz, or inert plastic. The pump, P2, pulls the sample and the diluent air past the inlet to the reactor. The mix of air and sample is controlled by valves V5 and V2, respectively. The flow of the diluted sample into the vacuum reaction chamber is controlled by V6. Valves V8 and V9 are manipulated to obtain optimum flow of oxygen through the ozone generator and to maintain near atmospheric pressure in the ozone generator. Atomic oxygen is generated as the ozone passes through the heated quartz tube. The chemiluminescence occurs within the inner tube as the two gas

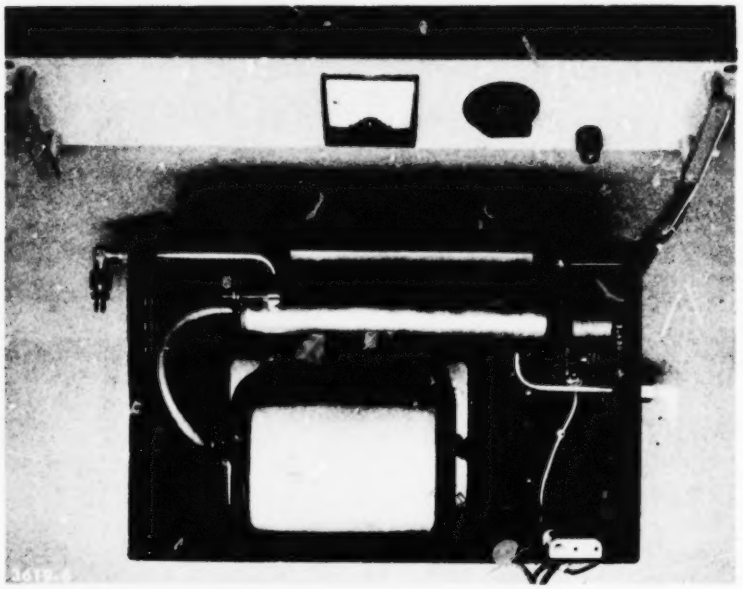


Figure 2. Ozone Generator

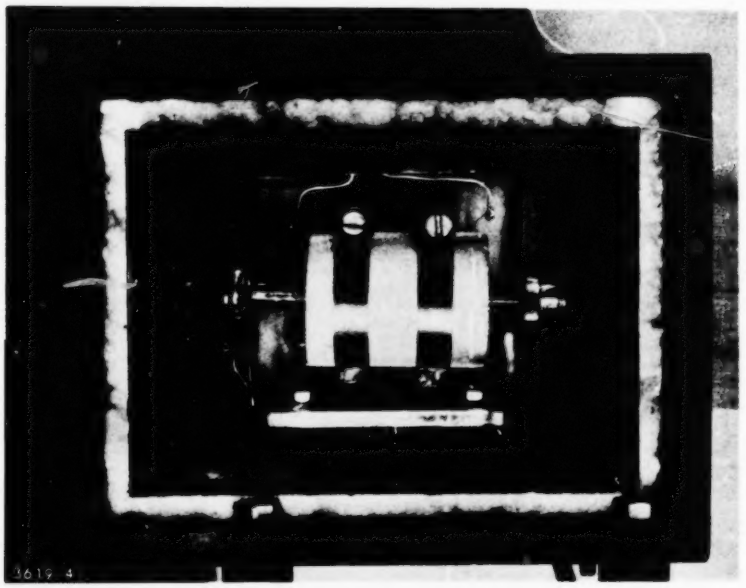


Figure 3. Thermal Decomposition Chamber

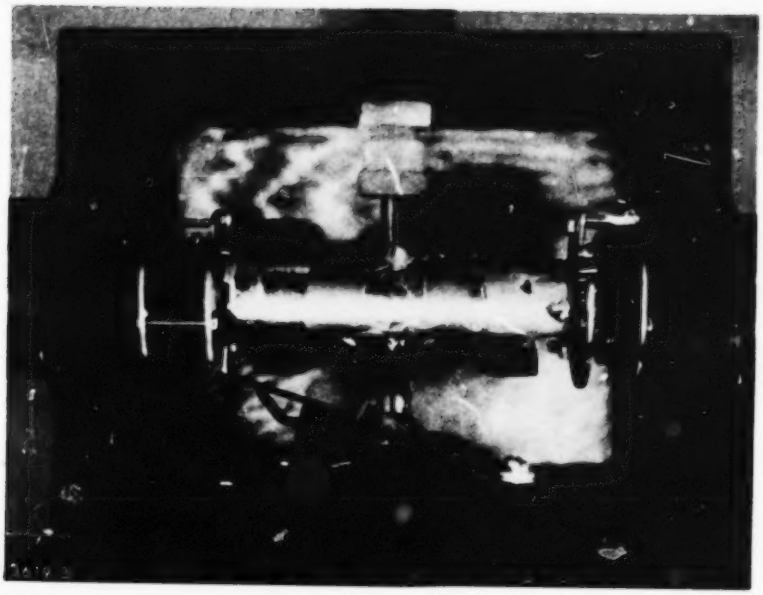


Figure 4. Reaction Chamber

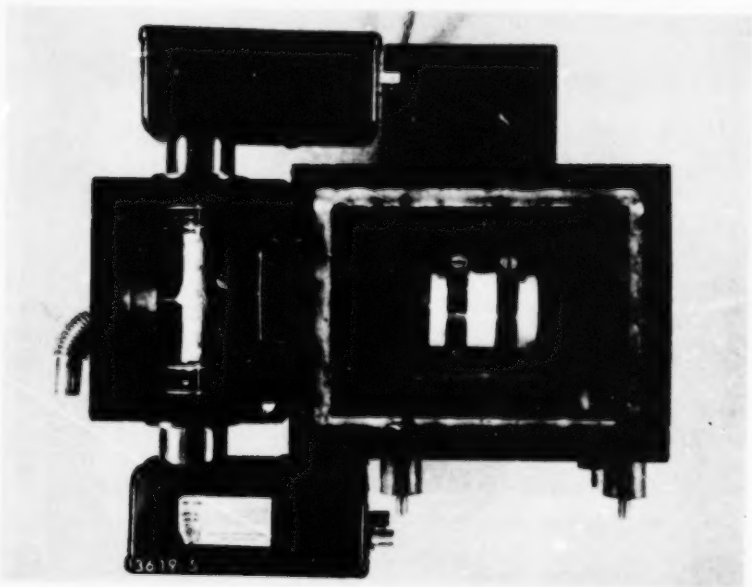


Figure 5. Detector Assembly

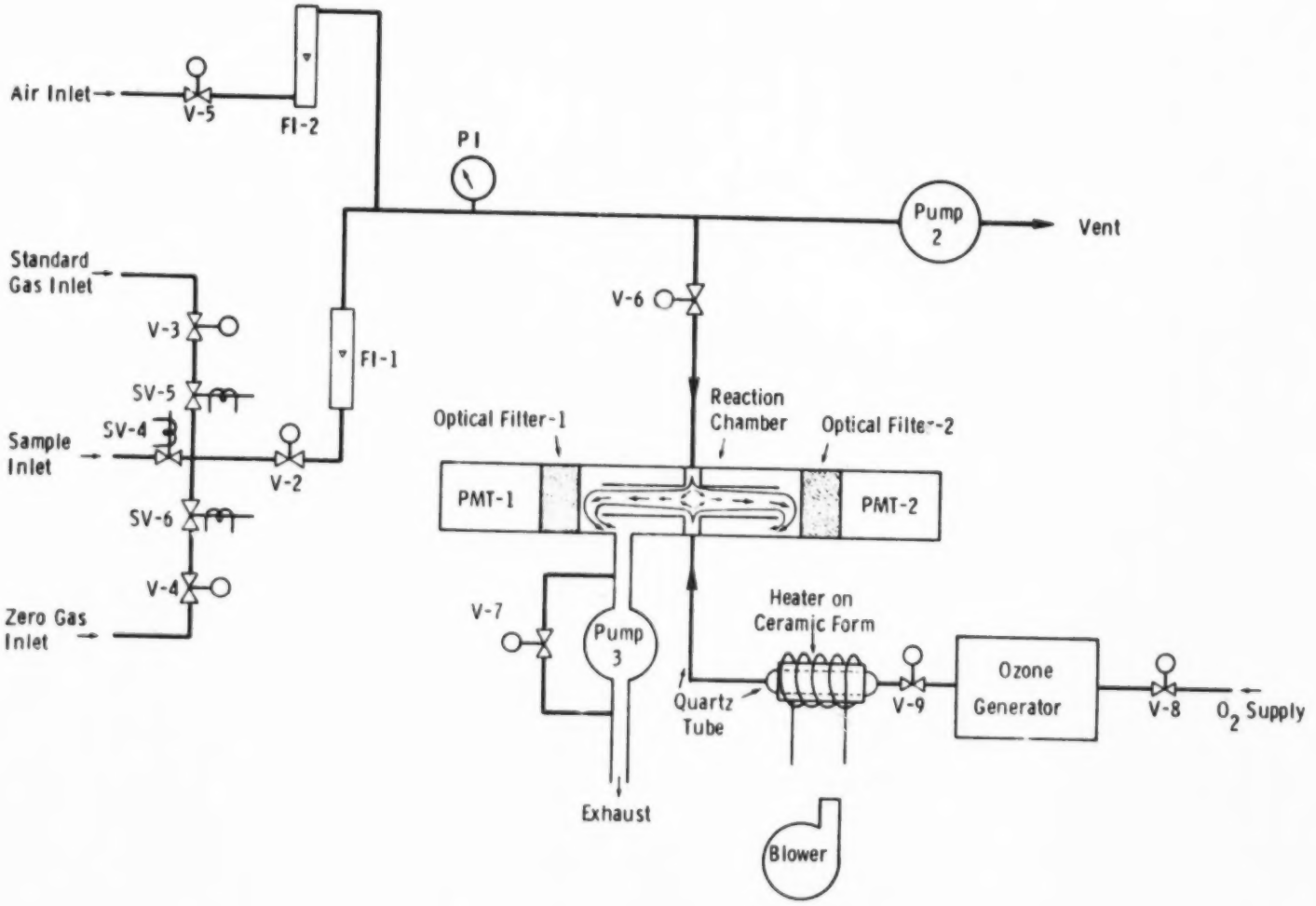


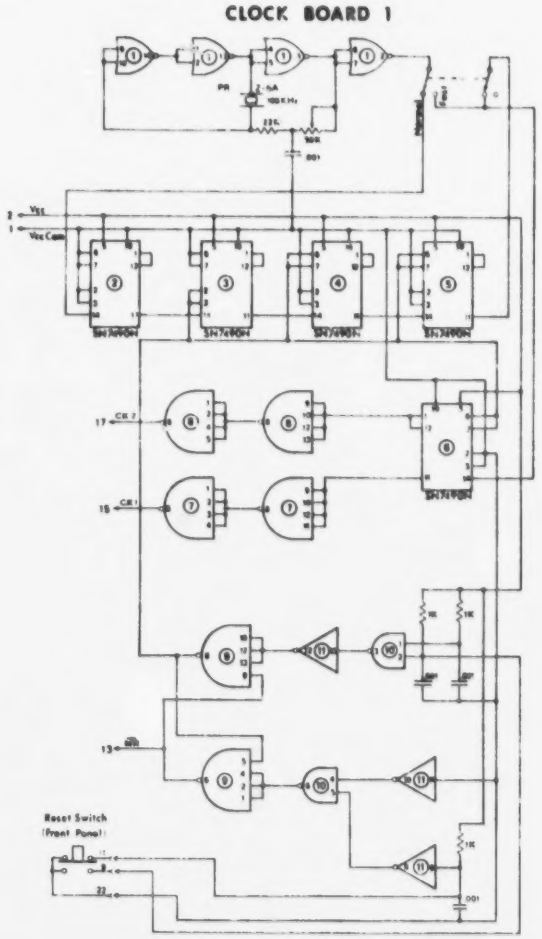
Figure 6. Pneumatic Schematic

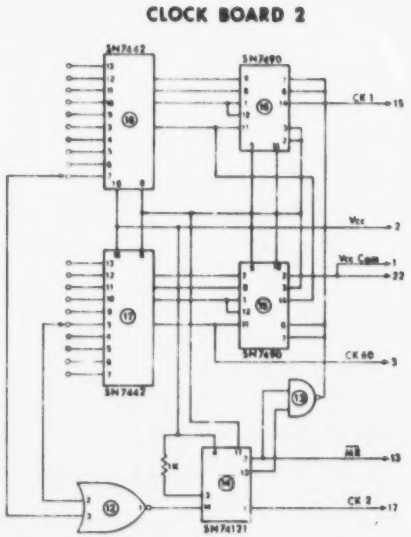
streams mix. The mixture remains within the field of both photomultipliers as it passes from the point of entry at the center through the inner tube to either end and back to the exit point at the center through the outer tube. The pressure can be controlled by the by-pass around the vacuum pump, P3.

Electronic Modification

The electronic circuit modifications were divided into three parts. First, the programmer modifications required some circuit changes but no major design. Second, the amplifier circuits required a complete redesign. Third, the connecting wiring required partial redesign.

Programmer - The programmer consists of a clock circuit (Figure 7), a logic circuit (Figure 8), and a solenoid driver circuit (Figure 9). The clock consists of a 100 kHz oscillator and a five-decade counter circuit for generating a one-second clock pulse. A second counter circuit is programmable for a divide by 1-99 counter to establish the basic time unit for the pin board programmer on the front panel. As wired, the basic time unit is 60 seconds. Thus, a function programmed to remain on 15 time units will actually have a 900 second duration. The programmer is designed to reset itself at a programmable time. The auto zero cycle can be programmed to occur at any time within the interval of the total cycle and to have any desired duration. The electronic auto zero function is on only during the last time unit (60 seconds) of the auto zero cycle. The standard gas cycle can be programmed to occur at the beginning of each Nth cycle where N is a number greater than 1. A typical program would have a auto zero cycle of 10 time units (600 sec.) occurring





I.C. No.	Vcc Pin No.	Ground Pin No.	
1	8	1	SP 380 A
7	14	7	SN 7440 N
8	14	7	SN 7440 N
9	14	7	SN 7440 N
10	14	7	SN 7400 N
11	14	7	SN 7404 N
12	14	7	SN 74L02 N
13	14	7	SN 7400 N

Figure 7. Clark Circuit Schematic

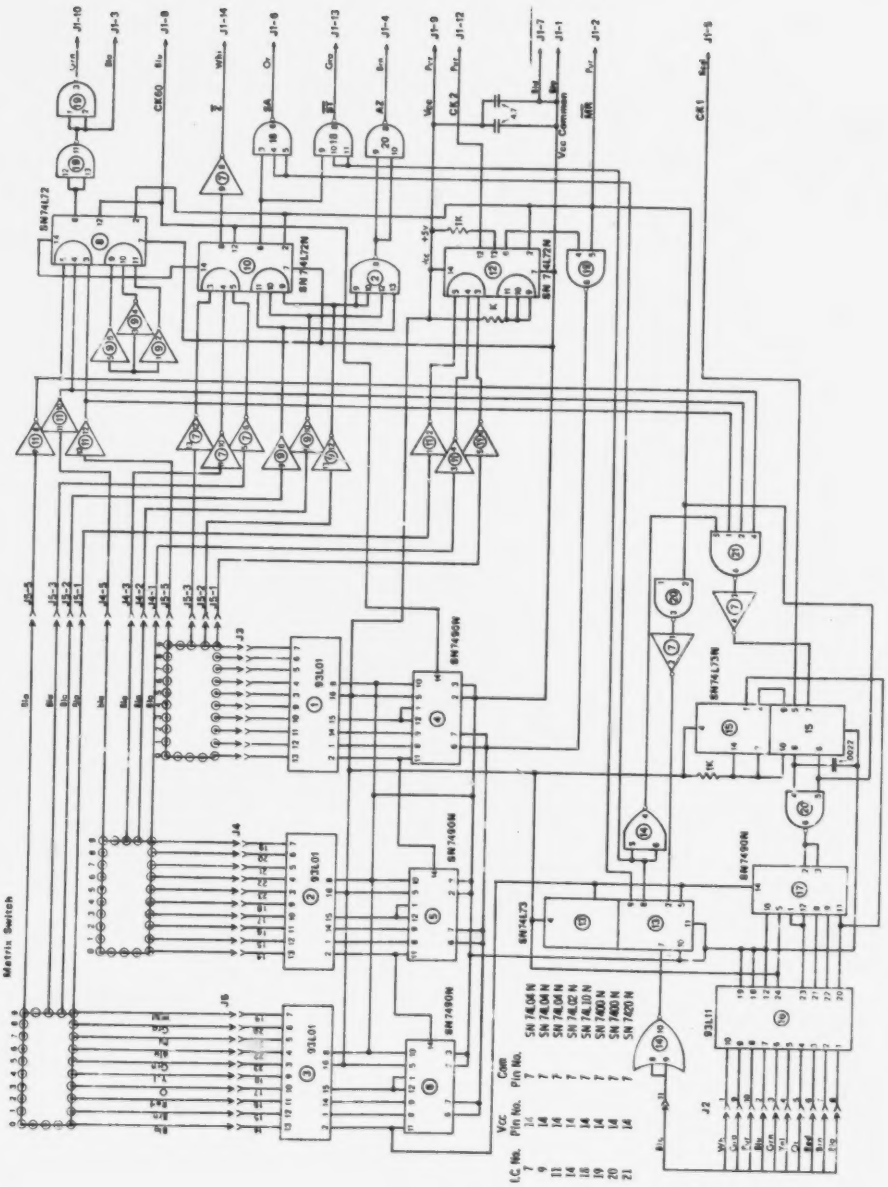


Figure 8. Logic Circuit Schematic

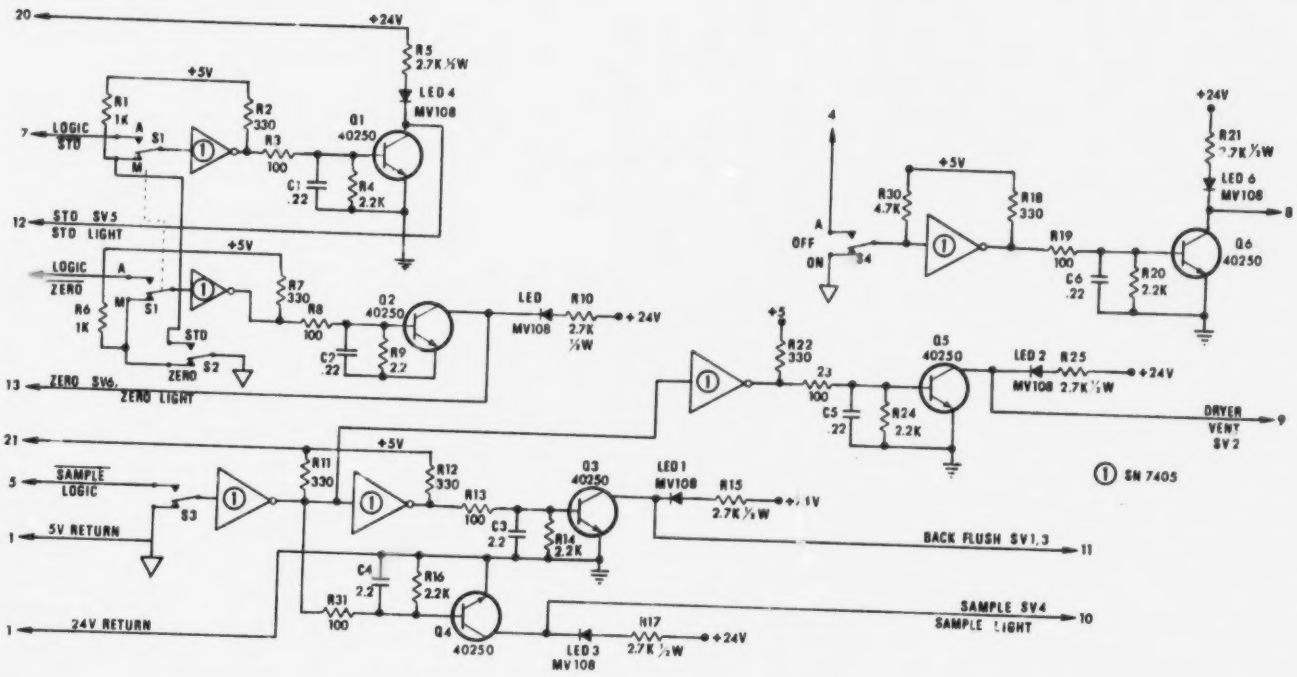


Figure 9. Solenoid Driver Circuit Schematic

each cycle of 240 time units (4 hours) with a 10 time unit (600 sec.) standard cycle each 6 cycles (24 hours).

Amplifier - The amplifier circuit was completely redesigned and new printed circuits made. Identical channels were provided for each of two photomultipliers. Because the intervals between the auto zero cycles were long, a digital memory circuit was incorporated to prevent drift normally associated with capacitor leakage in analog memory circuits. The circuit is shown in Figure 10. The amplifier consists of three stages. The first is a LM308A operational amplifier with adjustable gain and a front panel zero adjustment. The second stage is a LM301A with a front panel gain adjust and a zero control input from the auto zero circuit. The third stage is a LM201A amplifier with a switchable gain on the front panel and a zero adjustment on the printed circuit board. The output of the second stage also goes to the input of a LM201A acting as a comparator such that its output always has the opposite polarity of the second-stage amplifier and is much greater in magnitude. Therefore, when the second-stage amplifier output is not zero, the output of the comparator is large. The comparator drives a Schmitt trigger (SN7413N) which in turn drives a logic circuit controlling a two-stage, binary up-down counter whose digital output drives a digital-to-analog (D-A) converter (DAC372-8). Upon being enabled by a signal from the programmer or a switch on the front panel, a 100 pulse per second clock signal is routed through the logic circuit to the up-down counter, which counts up or down depending on the polarity of the comparator. The analog output of the D-A converter is fed to one input of the second stage LM301A such that the LM301A output is always driven toward zero. The system responds much as a slightly oscillatory servo system in that the LM301A output

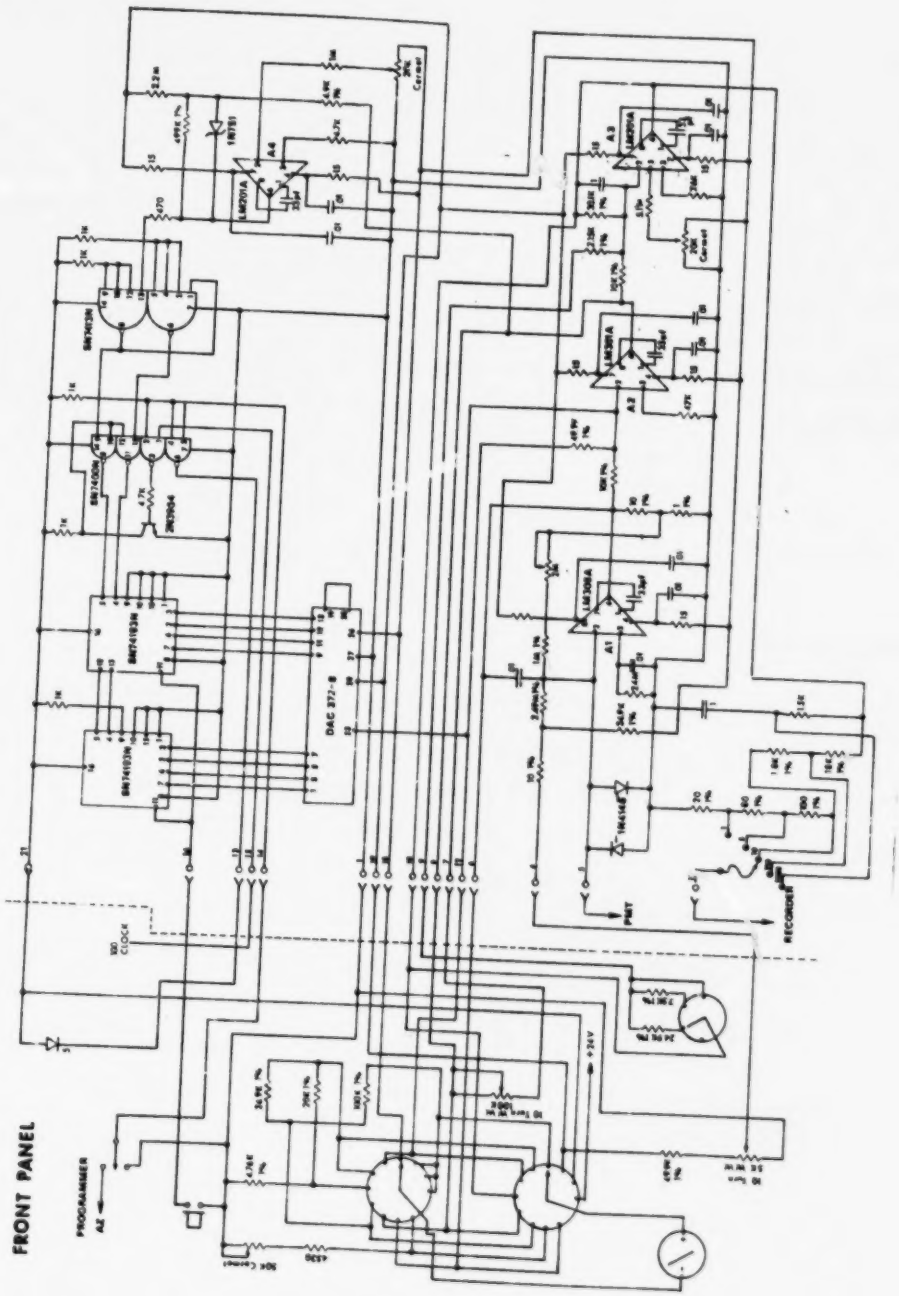


Figure 10. Amplifier Circuit Schematic

oscillates ± one bit around zero. By making one bit insignificantly small, the output of the LM301A can be forced to zero for all practical purposes. Upon removal of the auto zero signal, the counter is disabled, but it retains its digital output. Therefore, the analog zeroing signal from the D-A converter is maintained until the circuit is again activated.

Connecting Wiring - The connecting wiring was modified as required. A new harness was made for the front and rear interconnections and the mother board was cut and patched where necessary. The new wiring diagram is included in Figure 10.

EXPERIMENTAL WORK

Permeation Dryer

The ability of the Model PD-500-40 Perma Pure dryer to pass SO_2 and NO_2 unchanged was determined. Water vapor, NO_2 and SO_2 at various known levels of concentration were introduced into the sample inlet of the dryer while the outlet was monitored to detect losses in transient. It was found that significant losses were incurred unless the drying air in the outer shell was much dryer than the sample. Almost total loss of NO_2 was experienced under wet air conditions. However, no detectable change in SO_2 and only a small 1-2% change in NO_2 was found when dry air was used.

Oxygen Generator

The Orec Model 03V5-OM Ozonator failed to operate satisfactorily within the recommended input current range of 0-150 mA

but did function at 175-250 mA. Sustained operation at that level produced no detectable ill effects. It was found that the pressure affected the operation of the unit. Optimum performances seemed to occur at 0-2 psig.

The modification of the monitor was delayed for some time awaiting delivery of the optical filters. The 6500 ± 20Å filter was received and installed in mid-November 1972. A test was run to test the response to NO with the results shown in Figure 11. No effort was made to calibrate the instrument at that time since the 3400Å filter had not been delivered.

In view of the considerable delay in the delivery of the 3400Å filter, a Fish-Schurman UG-1 filter was ordered and received late in January 1973. After demonstrating that linear results could be produced by microwave excitation to produce atomic oxygen, an effort was again made to obtain positive results using the ozone/thermal decomposition method. Again, no detectable response was obtained for SO_2. The response to NO_2 is shown in Figure 11.

Although the UGI filter was inferior to the T-5, Infrared Industries filter, it was useful in evaluating the performance of the instrument. On February 1, 1973 an effort to detect SO_2 failed. The gain of the amplifiers was increased to a point where the noise level was detectable and the results tabulated in Table 1 were obtained.

As a result of the failure to detect SO_2, a test was devised using a microwave generator to generate atomic oxygen as shown in Figure 12. The results of tests are shown in Figure 13.

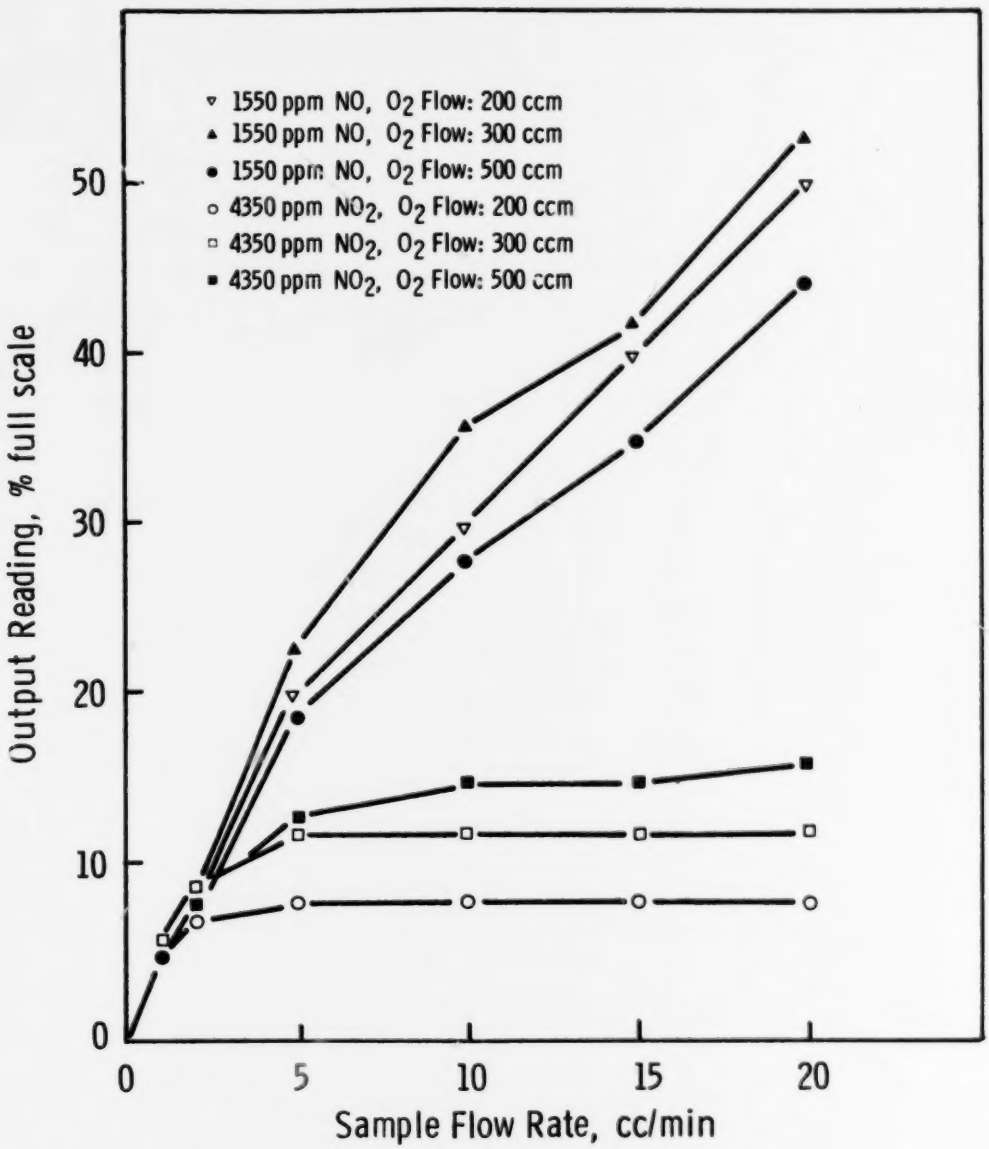


Figure 11. Response to NO and NO_2 with Ozone Generator

Table 1. RESPONSE TO NO, SO_2 WITH OZONE

Conditions:
Reaction Chamber Pressure: 1 - 5 torr
Ozone Generator Current: 250 mA
O_2 Flow Rate: 200 cc/min
Decomposition Heater Temperature: 800 - 900°C
Samples: 1550 ppm NO in N_2
280 ppm SO_2 in N_2
1050 ppm SO_2 in N_2

NO_x Filter: 6500 ± 50Å
SO_2 Filter: 3400 ± 50Å
(SO_2 filter transmission is appreciable above 6000A)
NO_x photomultiplier: EMI 9781-B
SO_2 photomultiplier: RCA 1p 28
NO_x gain: 0.50
SO_2 gain: maximum

State of Sample Input	NO_x Output, mV (1000 mV fs)	Flow Rate of Sample, cc/m	SO_2 Output mV
Ozone Gen. off No sample	± 5	0	± 15
Ozone Gen. on No sample	5 ± 5	0	5 ± 15
Ambient Air	30 ± 10	100	20 ± 20
NO	550 ± 10	100	110 ± 20
SO_2 (280 ppm)	30 ± 10	100	20 ± 20
SO_2 (1050 ppm)	30 ± 10	100	20 ± 20
SO_2 (1050 ppm) + NO	30 ± 10	50 ea.	30 ± 20
NO	250	50	50 ± 20
SO_2 (1050 ppm) + NO	30 ± 10	50 ea.	30 ± 20
SO_2 (1050 ppm) + NO	30 ± 10	50 NO, 5 SO_2	30 ± 20

Table 2. NO RESPONSE WITH OZONE

Conditions: Ozone Generator Current: 225 mA
Ozone Generator Chamber Pressure: 1.5 psig
Decomposition Heater Volts: 70
Sample: 1550 ppm NO in N_2
Span Gain: 4.00
Ozone Generator Input: O_2
Range Switch: 0-3000 ppm

Reaction Chamber Pressure, torr	O_2 Flow Rate, cc/min	Sample Flow Rate, cc/min	Output, % (full scale)
1.2	200	0	0
1.2	200	25	20
1.2	200	50	30
1.2	200	75	40
1.2	200	100	50
1.3	300	0	0
1.3	300	25	23
1.3	300	50	36
1.3	300	75	42
1.3	300	100	53
1.5	500	0	0
1.5	500	25	19
1.5	500	50	28
1.5	500	75	35
1.5	500	100	44

Table 3. RESPONSE TO NO_2

Conditions: Ozone Generator Current: 225 mA
Ozone Generator Chamber Pressure: 1.5 psig
Decomposition Heater Volts: 90
Sample - 4350 ppm NO_2 in N_2
Span Gain - 4.00
Ozone Generator Input - O_2
Range Switch 0 - 3000 ppm

Reaction Chamber Pressure, torr	O_2 Flow Rate, cc/min	Sample Flow Rate, cc/min	Output, % (full scale)
0	200	0	0
	200	5	5
	200	10	7
	200	25	8
	200	50	8
	200	75	8
	200	100	8
1.3	300	0	0
1.3	300	5	6
1.3	300	10	9
1.3	300	25	12
1.3	300	50	12
1.3	300	75	12
1.3	300	100	12
1.5	500	0	0
1.5	500	5	5
1.5	500	10	8
1.5	500	25	13
1.5	500	50	15
1.5	500	75	15
1.5	500	100	16

Table 4. RESPONSE TO SO_2 WITH MICROWAVE

Conditions: Sample: 3500 ppm SO_2 in N_2
Span Gain: 3.10
Range: 0-1000 ppm

Microwave Power, watts	O_2 Flow, cc/min	Sample Flow to Reactor, cc/min	Output Reading, % Full Scale
50	120	0	0
		5	18
		10	28
		20	43
50	153	0	0
		5	14
		10	27
		20	44
50	225	0	0
		5	10
		10	22
		20	45
75	120	0	0
		5	21
		10	32
		20	49
75	153	0	0
		5	17
		10	30
		20	50
75	255	0	0
		5	12
		10	25
		20	50

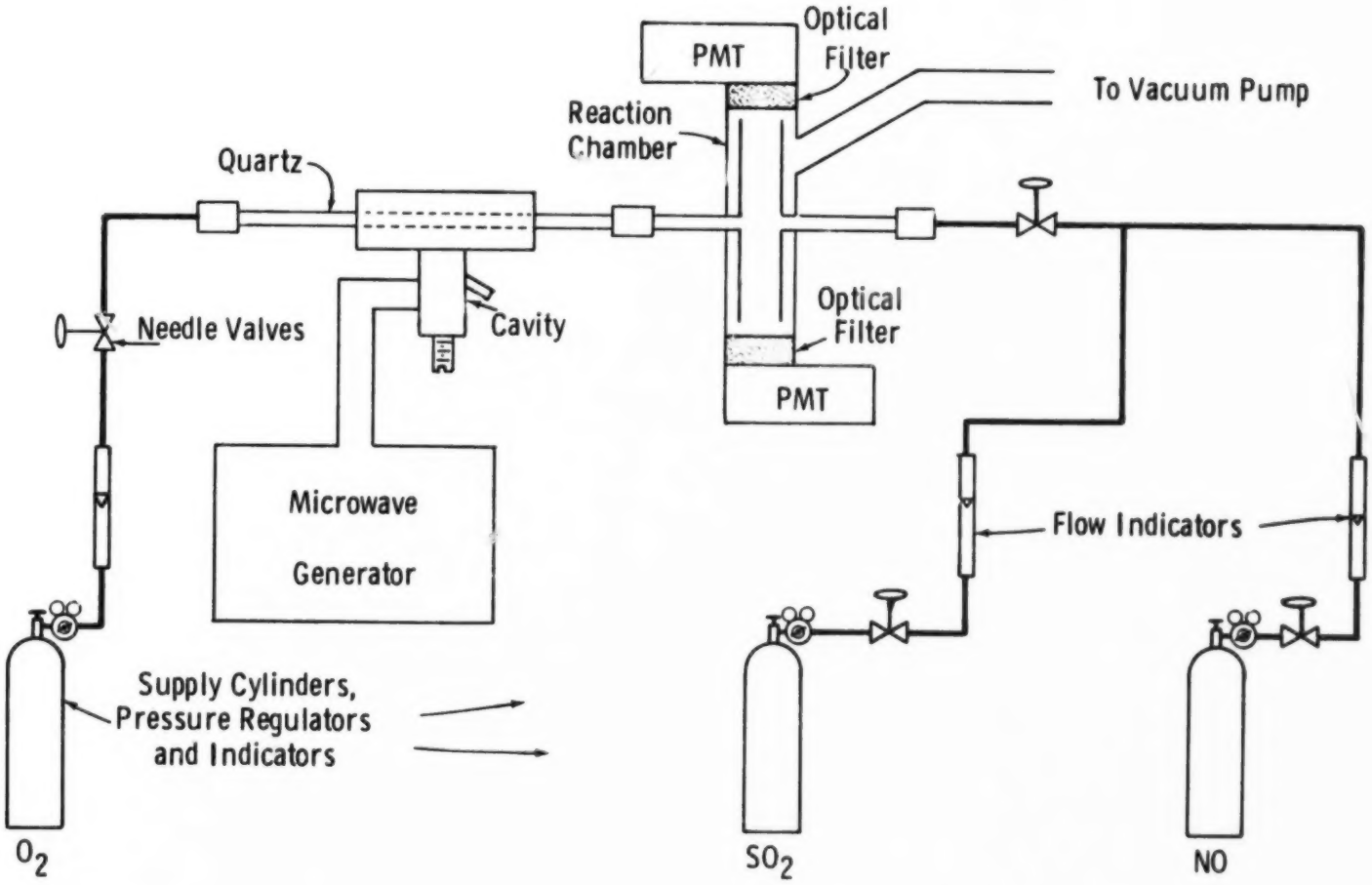


Figure 12. Schematic for Microwave Excitation

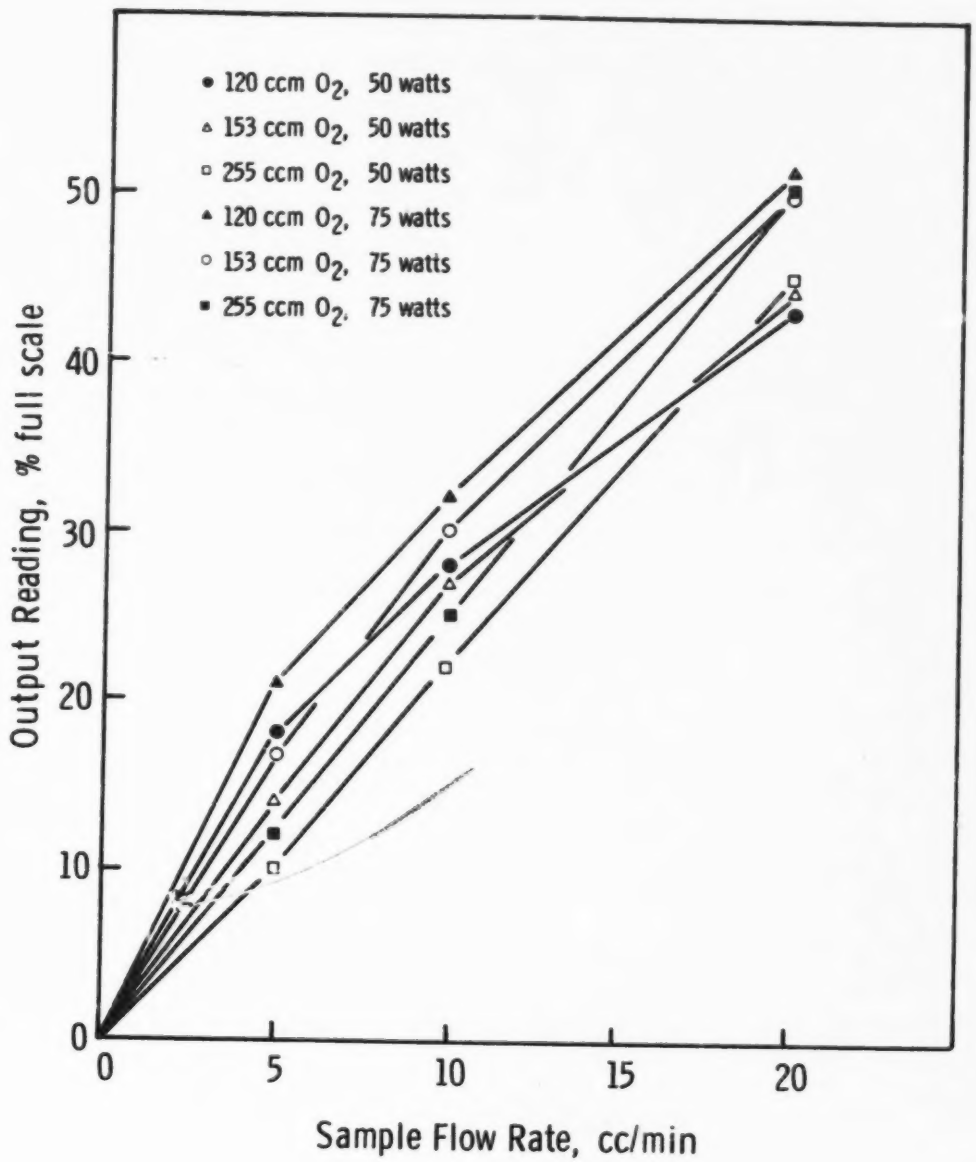


Figure 13. Response to SO_2 With Microwave Excitation

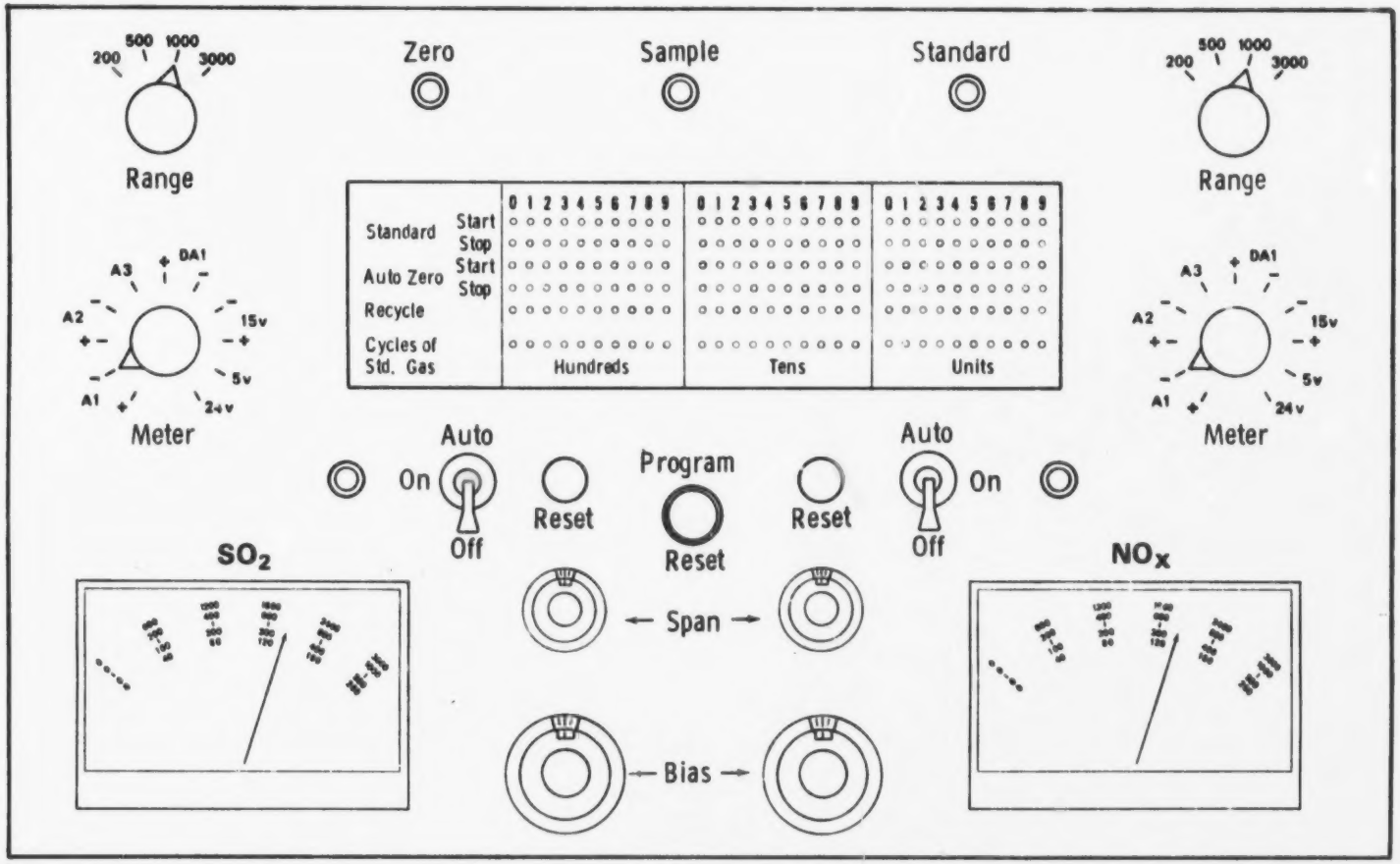


Figure 14. Front Control Panel

Further experiments results in configurations which produced linear results for SO_2 and NO_2 when using microwave excitation. Table 4 shows the effect of oxygen flow rate on the response to both SO_2 and NO.

APPENDIX

OPERATING INSTRUCTIONS

PROGRAMMING

Programming of the instrument is accomplished by means of the recessed pin board matrix switch on the front panel. See Figure 14. The five upper rows of pin holes control the normal cycle program except that the standard cycle occurs only as programmed by the lower row of pins.

The third row sets the start of the auto zero cycle and the fourth row sets the end of auto zero cycle. The fifth row sets the time at which the program cycle resets itself and starts over.

The first row sets the start of the standard cycle and the second row sets the end. However, the standard cycle only occurs as often as programmed by the lower row of pins. For instance, a pin in the sixth position of the lower row causes the standard cycle to occur once each sixth program cycle. The format for programming is reasonably straightforward. The basic time unit is one minute, and there are three decades on each row such that program cycles can be up to 998 minutes.

One peculiarity of programming is that the actual programmed time is one time unit less than the program on the board. Therefore, a one-hour time required a 061 pin setting.

AMPLIFIER

Each channel amplifier consists of a printed circuit board and various resistors and potentiometers on the front panel. See Figure 10. Each P.C. board contains three integrated circuit analog amplifiers for signal conditioning and one I.C. analog amplifier acting as a comparator which, together with various logic and counting and a digital to analog converter, comprises an automatic zero circuit.

The first amplifier stage, a high-input impedance LM308A, accepts the current signal from the anode of a photomultiplier tube. The gain this stage is set by a potentiometer on the P.C. board, such that its output is approximately five volts for a 3000 ppm sample. A ten-turn, 5K potentiometer on the front panel provides a suppression current for nulling any background current from the P.M.T. The second stage is a LM301A, the gain of which can be adjusted by the ten-turn, 100K span potentiometer on the front panel. The output of this stage is adjusted to provide five volts at its output, for a 3000 ppm sample. Zero adjustment of this stage comes from the output of a digital-to-analog converter in the automatic zero section. The third stage accepts the signal from the output of the second stage. This signal is amplified by an amount determined by the range switch on the front panel to provide one volt at the output for a sample containing the full scale concentration set on the range switch. Zero adjustment is made by means of a 20K trim potentiometer on the P.C. board.

A LM201 amplifier accepts the output of the second stage and generates a large output voltage of the opposite polarity. That output is accepted by a Schmitt trigger logic gate

which provides a switching action with very small hysteresis. The gate output routes a clock pulse to one of two inputs of an up/down counter, depending on the polarity of the second stage output, through another set of gates which turns the clock pulse train on or off, depending on the state of the command signal which is received through a switch on the front panel. That switch controls the auto zero circuit or connects it to the programmer which turns it on at the end of the auto zero cycle. A push-button switch resets the counters to mid range. The binary output of the counter is accepted by a DAC 372-8, eight bit digital-to-analog converter which supplies a zero signal to the input of the second stage. The action of the total circuit is such that when the auto zero circuit is on, the counter counts in a direction, up or down, to make the D-A converter output change in a direction to cause the second state output to decrease. Upon crossing zero, that output causes the count direction to change so that the circuit oscillates one to two bits around zero. By making the effect of the D-A converter output on the second state output small enough, that oscillation is insignificant. Thus, the circuit operates very much as a slightly oscillatory servo system. When the auto zero is turned off, the counter and D-A converter remain in their last state, thereby retaining the suppression current to the second amplifier stage input.

AUTOMATIC OPERATION

In the automatic mode, the programmer transmits logic level signals to the solenoid driver and automatic zero circuits. These signals are derived from the clock counters through decode and latching circuits, such that the automatic zero mode and the standard mode are programmable, as is the

frequency of the standard mode and the period of a program cycle. The logic is such that the sample mode is on at all times when neither the zero nor the standard mode is on.

In the sample mode, SV4, the sample solenoid, is activated allowing the sample to be drawn through the instrument, see Figure 6. The dryer vent valve, SV2, is also activated, see Figure 1, allowing the drying air in the sample conditioning probe to vent to atmosphere. A part of the gas passing through the instrument is bled through a needle valve, V6, into the reaction chamber where the pollutant reacts with atomic oxygen entering from the opposite side. If necessary, needle valve V5 may be adjusted to provide the required dilution of the sample by entering clean air into the stream.

Atomic oxygen is generated by passing molecular oxygen through an ozone generator at near atmosphere pressure and thermally decomposing the ozone as it passes through a heated zone at 800 - 900°C. The flow rate of the ozone/oxygen mixture is set by needle valve V9, which bleeds it into the vacuum chamber ahead of the heated zone. The mixture containing ozone and molecular, as well as atomic, oxygen then passes into the reaction chamber where it mixes with the sample and passes in either direction down the inner tube of the reaction chamber to the end and back to the middle where it exits to the vacuum pump, P3.

Upon initiation of a zero cycle, the dryer vent solenoid valve and the sample solenoid valve are deactivated, thereby blocking entrance of the sample to the instrument and blocking the exit of the drying air from the permeation dryer in the sample probe. Simultaneously SV1 and SV3 activate allowing an increased flow of drying air to be pumped in a reverse direction through the permeation tube and input filter to

vent into the stack. Also SV6 activates allowing a clean dry air flow into the instrument. Needle valve, V4, is adjusted to maintain the same flow through the instrument as was present during the sample mode of operation. During the last minute of the automatic zero mode, the electronic auto zero circuit is activated causing the output of the amplifier to read zero. That level of suppression is then maintained until the next automatic zero mode.

Upon initiation of the standard mode, the sequence is identical to that described for the automatic zero mode, except that SV5 is activated, rather than SV6, allowing a standard gas of known concentration to enter the instrument and the electronic automatic zero circuit is not activated. Since the composition of the standard gas is known, span adjustments may be made to compensate for any changes since the last such adjustment, or the changes may be noted or displayed on a recorder for later computations.

ELECTRICAL

Upon receipt of the instrument, it should be checked for damage in shipping. Check all printed circuit cards and connectors to see that they are seated well. Connect the probe to the monitor by means of the cable with ampherol connectors furnished. Plug all A.C. line plugs into the power distribution panel in the top rear of the monitor. If independent on-off control is desired, use plugs with switches adjacent. Supply 115V, 60 Hertz, to the male receptacle at the rear. Turn on all applicable power switches.

PNEUMATIC

Connect sample line between the probe and the monitor. Connect zero gas, standard gas, and oxygen lines to the monitor and to the appropriate bottles with regulators. Adjust oxygen flow to 100 CC/min. Connect vacuum pump to outlet at rear of instrument and turn on.

ELECTRONIC

Adjust Powerstat at rear of monitor for 225 milliamperes ozone generator current. Allow 15 minutes for thermal decomposition heater to stabilize. Set up desired program and reset programmer by pushing the reset switch.

INITIAL CALIBRATIONS

Provide a calibration sample of known composition and set range switch to appropriate range. Set up a long standard mode period following an automatic zero mode. Allow a sufficient response time (5 to 10 minutes); then switch the meter to read up-scale on A1 and adjust the trim potentiometers on the P.C. boards to 5 volts per 3000 ppm of the pollutants. For example, 1500 ppm should provide 2.5 volts at A1. The meters are calibrated for approximately 10 volts, full scale. Next, switch to A3 and adjust the span potentiometers on the front panel to provide the correct readings on the meters. Re-program for the desired mode of operation and reset the programmer.